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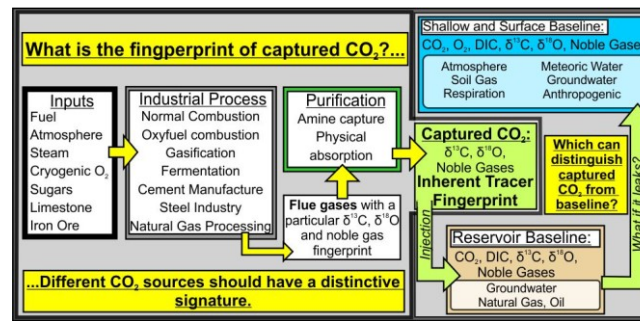
Inherent tracers for carbon capture and storage in sedimentary formations: composition and applications

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Abstract

Inherent tracers - the “natural” isotopic and trace gas composition of captured CO₂ streams – are potentially powerful tracers for use in CCS technology. This review outlines for the first time the expected carbon isotope and noble gas compositions of captured CO₂ streams from a range of feedstocks, CO₂-generating processes and carbon capture techniques. The C-isotope composition of captured CO₂ will be most strongly controlled by the feedstock, but significant isotope fractionation is possible during capture; noble gas concentrations will be controlled by the capture technique employed. Comparison with likely baseline data suggests that CO₂ generated from fossil fuel feedstocks will often have $\delta^{13}\text{C}$ distinguishable from storage reservoir CO₂. Noble gases in amine-captured CO₂ streams are likely to be low concentration, with isotopic ratios dependant on the feedstock, but CO₂ captured from oxyfuel plants may be strongly enriched in Kr and Xe which are potentially valuable subsurface tracers. CO₂ streams derived from fossil fuels will have noble gas isotope ratios reflecting a radiogenic component that will be difficult to distinguish in the storage reservoir, but inheritance of radiogenic components will provide an easily recognisable signature in the case of any unplanned migration into shallow aquifers or to the surface.



1. Introduction

1.1 The need for CCS

The link between atmospheric concentrations of anthropogenically produced CO₂ and global warming is unequivocal¹⁻⁴ and CO₂ emissions must be drastically reduced, and eventually stopped, if we are to avoid catastrophic, irreversible climate change. Carbon Capture and Storage (CCS) features prominently in all scenarios that consider timely and feasible reductions in CO₂ emissions^{1,5}. Importantly, CCS is the only technology that can substantially reduce carbon emissions from industrial processes such as chemical synthesis and steel production. Climate models are increasingly relying on the use of negative emissions to limit global average temperature rise to 2 °C and include large amounts of bio-energy combined with CCS (BECCS), as this is the only feasible, industrial-scale negative emissions technology currently available⁶.

Carbon capture in the context of this review involves removal of CO₂ from the flue gases of point-source emitters, such as power stations and industrial plants, to produce a stream of high concentration CO₂. Current well-developed capture techniques are often classified into one of three categories. (1) "Amine capture", also referred to as "post combustion capture" because it was originally envisaged to be applied most often to fossil fuel or biomass combustion-fired power stations, removes CO₂ from a gas stream by chemical reaction of the CO₂ with an amine solvent (with or without the use of membranes), and is already widely used by the hydrocarbon industry to remove CO₂ from produced natural gas⁷. (2) "Oxycombustion" or "oxy-fuel combustion" produces a high CO₂ purity flue gas by burning fuel in an oxygen rich atmosphere, rather than air, and recycling the flue gas

into the combustion chamber. (3) “Pre-combustion capture” collects the CO₂ produced during gasification processes and is so named for the potential to generate hydrogen fuel, which can be combusted without producing CO₂ to produce electricity. These general carbon capture terms were developed in the context of CCS being most readily applied to electricity generation (hence the focus on pre- or post-combustion). In reality, these capture techniques are already applied to a much wider range of industrial activities, such as natural gas processing, Synfuel production and chemical / fertiliser manufacture (see Section 3), and so classification according to the stage of electricity generation is no longer appropriate. As such, we use the terms “amine capture”, “oxyfuel” and “gasification” when discussing these three different types of capture technique. Additional pressure-based adsorption techniques onto solid adsorbents (e.g. pressure-swing adsorption) or organic solvents are also used during gas purification, especially as part of the gasification processes.

The efficiency of CO₂ capture and the purity of the captured CO₂ stream vary between ~95% and 99.9%^{2,8} depending on the capture method, post capture clean-up and specific conditions employed. Industrial specifications require a CO₂ purity of >95% for transport and storage, to maximise density and avoid problematic phase changes, and so end-product CO₂ streams tend to contain 90-99% CO₂, with minor to trace amounts of N₂, hydrocarbons, H₂S, NO_x, SO_x, O₂, H₂O and noble gases (especially Ar)⁷⁻⁹.

1.2 The need for CO₂ tracers

Commercial scale carbon-storage projects will be required by governmental regulatory bodies to monitor CO₂ injected for storage and mitigate any unplanned behaviour, such as migration out of the storage reservoir (leakage) or to the surface (seepage), in the storage complex¹⁰. Furthermore, being able to trace the migration and reactions of injected CO₂ in the subsurface is fundamental to the continual assessment of injectivity, identification of CO₂ trapping mechanisms and quantification of storage capacity, all of which need to be well understood and characterised to ensure storage security.

Geophysical techniques, while useful monitoring tools, remain limited in their ability to quantify CO₂ pore space saturation and dissolution at high spatial resolution^{11–13}. Seepage rates of 0.001 - 0.01% per year are generally considered acceptable on a climate accounting basis, amounting to a loss of ~1% of the injected CO₂ over 100 years, a target adopted by the U.S. Department of Energy^{14,15}. Conclusive detection of such seepage rates by measurement of CO₂ concentrations remains problematic due to natural background CO₂ fluctuations. A potential solution to this problem is the use of geochemical tracers, detectable at low concentrations due to their low background level in the atmosphere or storage complex. Addition of geochemical tracers for environmental monitoring and interpretation of reservoir dynamics is a long-standing practice in the hydrocarbon industry, with perfluorocarbon tracer compounds (PFTs)¹⁶, tritiated and perdeuterated CH₄ and H₂O, freons, sulphur hexafluoride (SF₆)¹⁷ and noble gases such as Kr and Xe¹⁸ proving to be particularly useful tracers.

Tracers can be classified in terms of their relationship to the injected CO₂ as 1) added tracers (substances added to the CO₂ stream prior to injection, e.g. SF₆), 2) inherent or natural tracers (substances already present in the CO₂ stream or the isotopic composition of the CO₂ itself), or 3) indirect tracers (changes to baseline values resulting from interaction of the CO₂ with the natural environment, e.g. pH or cation content due to mineral dissolution)¹⁹. Adding geochemical tracers to injected CO₂ can facilitate detailed monitoring and modelling of CO₂ storage, but concerns remain regarding the economic cost of tracers in commercial scale storage sites, the possibility of increased background (lower sensitivity) / site contamination, and the environmental impact of such compounds^{17,20–22}. PFTs and SF₆, in particular, are potent greenhouse gases with atmospheric residence times of 1000s of years^{17,22}.

Using the isotopic and trace element geochemistry of the injected CO₂ itself as a tracer has the potential to facilitate in-reservoir tracing and leakage monitoring with minimal economic and environmental impact compared with added tracers. Furthermore, Article 12.1 of the EU directive on

CCS states that “no waste or other matter may be added for the purpose of disposing of [the CO₂]”¹⁰; while provision has been made in the directive for allowing the addition of tracers, these require consideration on a case-by-case basis and so use of inherent CO₂ tracers may help to simplify applications for CO₂ storage permits.

Here, we describe the inherent tracers which will be most useful for fingerprinting and monitoring CO₂ during storage, summarise the currently available information regarding inherent tracer signatures in both captured CO₂ and potential storage reservoirs, and highlight the further research necessary to facilitate the application of inherent tracer geochemistry to CCS. As we will show, the feasibility of using inherent tracers for measuring, monitoring and verification (MMV) depends on a number of variables, including the baseline composition of reservoirs and overburden of interest and the inherent tracer composition of the captured CO₂ stream. These will vary extensively depending on a number of factors and hence specific discussion of detection limits of the inherent tracers we describe is out of the scope of this review.

2. Inherent Tracers

For tracers to be effective, their compositions must be distinct from that of the storage site, including the host reservoir, overburden and local atmosphere. In this section we provide a brief background to and highlight further information on the isotope and trace gas systems that may be used as inherent tracers.

2.1 CO₂ Isotopic composition

The stable isotopes of C and O of injected CO₂ are an obvious potential tracer and have been successfully used in a number of projects to identify CO₂ migration and quantify pore space saturation and dissolution of CO₂ (see Section 6). Much of this work and background theory relevant to CCS has recently been summarised in a number of review papers^{12,19,23–26}. However, the isotopic composition

of the captured CO₂ itself, has received less attention, which we address in Section 3. For this review, we concentrate on using C-isotopes as a means of fingerprinting the injected CO₂. While O-isotopes of captured CO₂ may be a useful, quantitative monitoring tool¹¹, rapid equilibration of O-isotopes between CO₂ and water²⁷ means that the O-isotope composition of CO₂ will be controlled by any volumetrically significant water it interacts with; as a result, the O-isotope composition of CO₂ is expected to change significantly after injection into the storage reservoir and so not provide a diagnostic tracer of the CO₂ itself. Hence O-isotopes are not discussed in detail in this review.

For context, the range of isotopic compositions occurring in nature are shown in Figure 1 with details provided in Supplementary Data Table S1. C-isotope values are presented in δ¹³C relative to Vienna Pee Dee Belemnite (V-PDB), where

$$\delta^{13}\text{C} \text{ ‰} = \left(\frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}}}{(^{13}\text{C}/^{12}\text{C})_{\text{reference}}} - 1 \right) \times 1000$$

Isotope fractionation, enrichment factors (ε), and conversion between isotopic values relative to different standards are covered in detail in recent review papers which we refer interested readers to^{12,19,23–26}.

2.2 Noble gases

Noble gases (He, Ne, Ar, Kr, Xe) are particularly useful for tracing interaction of gases with fluids due to their unreactive nature and Henry's Law controlled solubility; in general, solubility increases with elemental mass and decreases with increasing temperature. Noble gases will preferentially partition into gas > oil > fresh water > saline water, and so mixing and migration of different fluids and gases in the subsurface may lead to multiple re-equilibration events that result in elemental fractionation of the noble gases^{28,29}. Hence, noble gases are being increasingly used to identify and quantify hydrocarbon migration pathways from modelling the elemental fractionation that occurs during partitioning between water, oil and gas^{30,31}. Noble gases in the subsurface can be considered a mixture

of three components³²: 1) Atmospheric derived noble gases, introduced to the subsurface by equilibration with meteoric water and recharge; 2) radiogenic noble gases produced in situ by decay of radioactive elements; 3) terrigenous fluids originating from defined geochemical reservoirs. Two common terrigenous components in sedimentary formations are crust and mantle. Mantle noble gases are enriched in ³He, with ³He/⁴He as high as 70 R_A (R_A being ³He/⁴He of atmosphere, 1.339 x 10⁻⁶) while crustal noble gases are enriched in radiogenic noble gases (⁴He and ⁴⁰Ar) and have ³He/⁴He <0.7 R_A³². In subsurface fluids a distinction exists between radiogenic and crustal components; the terrigenous crustal component is derived from radioactive decay, but represents the cumulative accumulation in the host rock, and is thus controlled by the age and chemistry of the geological formation hosting the fluid and the openness of the system, while the radiogenic component is added to the fluid by in situ radioactive decay and is thus a function of the host formation chemistry and fluid residence time³². Summaries of noble gas data relevant to CCS are shown in Table 1.

3. Geochemistry of the captured CO₂ stream

Two sources of information are available to assess the likely composition of the captured CO₂ stream: 1) a limited number of direct measurements on captured CO₂, and 2) hypothetical considerations of the feedstocks and processes involved in CO₂ generation. We analyse this information to draw conclusions about the range of CO₂ compositions that can be expected for different feedstocks and processes, which are summarised in Table 2. Further information regarding δ¹³C and noble gas content of a range of relevant feedstocks are provided in the Supplementary Information.

3.1 Direct measurement of the captured CO₂ stream.

CCS projects have reported captured CO₂ stream data from two oxy-combustion plants, three Synfuel / hydrogen production plants, two fertiliser manufacturers, one natural gas processing plant and one unknown combustion source. δ¹³C has been the most widely analysed tracer in captured CO₂ to date, giving a wide range of values from -51 to -4.7 ‰. Limited noble gas data is available for CO₂ streams

from fertiliser and oxyfuel plants. The limited available data is consistent with theoretical considerations discussed below, but the uncertainties involved (most often relating to the precise feedstock composition) hinder robust predictions of captured CO₂ stream chemistry and more studies are needed to clarify the $\delta^{13}\text{C}$ of captured CO₂.

3.2 Fuel combustion for energy production

Power stations are some of the largest point-sources of CO₂ emissions in the developed world making them obvious targets for CCS. In most cases, power is generated by combustion of material, often fossil fuels but with an increasing use of biomass, to drive a turbine and generate electricity. Capture of combustion-produced CO₂ will be either via amine capture or oxyfuel methods.

3.2.1 Carbon isotopes:

For CO₂ derived from fossil fuel combustion, Widory³³ identified ¹³C depletion in the CO₂ relative to the fuel, amounting to $\delta^{13}\text{C} \sim -1.3 \text{ ‰}$ for a range of fossil fuel types (solid, liquid, gas). More recent work has measured $\delta^{13}\text{C}$ during coal combustion and found that resulting CO₂ has $\delta^{13}\text{C}$ between -2.39 and +2.33 ‰ relative to the coal feedstock³⁴. $\delta^{13}\text{C}_{\text{CO}_2}$ of -46.2 ‰³⁵ has been reported for CO₂ derived from combustion of natural gas, which is consistent with (the admittedly wide range of) expected values (Figure 1) but the capture method was not reported.

For biomass, complete combustion of C3 and C4 plants produces CO₂ with the same C-isotope composition of the bulk plant, but partial combustion of C4 plants may result in ¹³C enrichment of the CO₂ (up to +4 ‰ at 3% combustion)³⁶. The C-isotope signature of CO₂ produced by burning biomass will therefore depend on the specific feedstock and the efficiency of the combustion process. Given the higher temperatures associated with oxy-combustion, we might expect a higher efficiency of biomass combustion compared to normal combustion and so no isotopic fractionation would be expected. Reported $\delta^{13}\text{C}$ of CO₂ from oxy-combustion of natural gas (-40 ‰, Rouse CCS Project³⁷) and

lignite (-26 ‰, Ketzin CCS project, see supplementary Table S2) are consistent with expected values (-61 to -21.3 ‰ and -31.3 to -21.3 ‰, respectively -Table 2).

3.2.2 Noble gases:

To the best of our knowledge, very little data is available on the noble gas content of combustion gases. Noble gases in combustion flue gases will be derived from the material being combusted and from the combustion atmosphere (air for normal combustion, cryogenic oxygen for oxyfuel). Concentrations of most noble gases in hydrocarbons are generally two to three orders of magnitude lower than in air (Table 1) and so atmospheric noble gases are expected to dominate. A radiogenic or terrigenous isotopic component might be resolvable in hydrocarbon-derived CO₂ due to elevated ⁴He in fossil fuels.

For oxyfuel, additional heavy noble gases (Ar, Kr, Xe) may be introduced with the cryogenically purified O₂. CO₂ injected at the Rouse CCS project was derived from oxy-combustion of natural gas³⁷. The source natural gas fuel was enriched in ⁴He and depleted in ²⁰Ne, ³⁶Ar, ⁴⁰Ar, and ⁸⁴Kr relative to air³⁷; the resulting CO₂ remained enriched in ⁴He and depleted in ²⁰Ne relative to air, but Ar isotopes had concentrations similar to air and ⁸⁴Kr was enriched by an order of magnitude compared to air³⁷. Enrichments of Ar (up to 2%) in oxyfuel captured CO₂ have also been observed during oxyfuel pilot experiments⁸, despite distillation procedures designed to remove inert gases⁷.

3.3 Gasification processes / Synfuel production / Pre-combustion CO₂ capture.

Here we use the term “gasification processes” to refer to the range of reactions used to generate Syngas (H₂ and CO) from a variety of fuel stocks. Syngas can be further processed by Fischer-Tropsch reactions to create a range of chemicals and synthetic fuels (Synfuels), including synthetic natural gas (SNG) and Fischer-Tropsch liquid fuels. These chemical reactions are described in the supplementary information.

227

228 Syngas is generated by a two stage chemical reaction. At the first stage, carbon monoxide (CO) and H₂
229 are produced from the feedstock, via either steam reforming or partial oxidation, followed by addition
230 of steam to stimulate a “shift reaction” that converts CO to CO₂, generating more H₂⁷. For synfuel
231 production the syngas stream is passed through a synthesis reactor where CO and H₂ are catalytically
232 converted to the desired chemical⁷. CO₂ from the entire process is captured both upstream and
233 downstream of the synthesis reactor and the captured CO₂ will be a combination of CO₂ generated
234 from different gasification stages, with a decreased input from the shift reaction as CO is used in
235 Fischer-Tropsch reactions. The resulting CO₂ is removed from the gas stream by either chemical
236 solvents (e.g. amine capture) or physical solvents (e.g. cold methanol)⁷.

237

238 **3.3.1 Carbon-isotopes:**

239 Fractionation of C-isotopes during gasification is likely due to increased bond strength of ¹³C-¹²C
240 compared to ¹²C-¹²C, resulting in ¹³C depletion in low molecular weight gases and ¹³C enrichment in
241 heavy residues like tar and vacuum bottoms³⁸. C-isotope ratios will be $\delta^{13}\text{C}_{\text{CO}} < \delta^{13}\text{C}_{\text{CH}_4} < \delta^{13}\text{C}_{\text{hydrocarbons}}$
242 $< \delta^{13}\text{C}_{\text{coal}} < \delta^{13}\text{C}_{\text{char}} < \delta^{13}\text{C}_{\text{CO}_2}$ at typical gasification temperatures (> 1000°C)^{39–41}. This suggests that any
243 CO₂ produced by incomplete reactions in the first stage of gasification is likely to be enriched in ¹³C
244 compared to the original feedstock, while the resulting CO will be depleted in ¹³C. This agrees with
245 experimental results from underground coal gasification plants^{38,40,42}, and natural gas generation via
246 pyrolysis of coal and lignite^{43,44}, which produced CO₂ enriched in ¹³C by 2-10 ‰ relative to the
247 feedstock. Conversely, CO₂ generated from CO via the shift reaction will be depleted in ¹³C. In a
248 simplistic scenario, all CO₂ resulting from gasification will be derived from the shift reaction and so we
249 could expect CO₂ captured from Syngas plants to be the same as or isotopically lighter than the
250 feedstock, depending on the efficiency of the gasification reactions and proportion of feedstock not
251 converted to Syngas. For synfuel and F-T plants, the ¹³C depleted CO will be used in chemical synthesis
252 and so early-generated, CO₂ slightly enriched in ¹³C will dominate. In reality, gasification of solid fuels

is likely to produce CO₂ and CH₄ in addition to CO and H₂, and so the isotopic composition of resulting CO₂ will depend on the proportions of ¹³C-enriched, early-produced CO₂ and ¹³C-depleted, shift-reaction CO₂. It is thus difficult to precisely predict the C-isotopic composition of CO₂ captured from syngas and synfuel plants. However, it is likely that the various fractionation and mixing processes will average out, giving CO₂ with an isotopic composition similar to, or slightly more ¹³C-depleted than the feedstock for syngas plants, and similar to or slightly more ¹³C-enriched than the feedstock for chemical and synfuel plants.

One of the sources of CO₂ injected at the Ketzin project was reportedly a by-product of hydrogen production⁴⁵ at an oil refinery⁴⁶. This CO₂ has δ¹³C ~-30.5 ‰⁴⁶ (Table S2) which is indistinguishable from the range of δ¹³C values expected for oil (-18 to -36 ‰, Table 2). CO₂ injected in the Frio project was derived from a refinery in Bay City, Texas, and the Donaldsonville fertiliser plant, Louisiana⁴⁷. Reported δ¹³C of the injected CO₂ was -51 to -35 ‰⁴⁸. While the end-member δ¹³C compositions were not reported, the values are consistent with those for natural gas (fertiliser plant) and oil (refinery) (see Table 2 and Figure 1). CO₂ captured from the Scotford Bitumen Upgrader, Canada, was derived from hydrogen production and purified using amine capture⁴⁹; most hydrogen production in the region is produced using steam methane reforming⁵⁰. The captured CO₂ has δ¹³C of -37 ‰⁵¹, which is within the range of δ¹³C values for natural gas. While the range of possible feedstock compositions is too wide to be conclusive, this data is consistent with our above predictions. The CO₂ injected at Weyburn is generated via coal gasification at the Great Plains Synfuel Plant, North Dakota, USA, and has a δ¹³C of -20 to -21 ‰⁵². This is indistinguishable from the (wide) range of δ¹³C for coal of -30 to -20 ‰ (Table 2). Data are not available for the coal and lignite used in the Synfuel plant, but coals and lignite from North Dakota have δ¹³C between -25 and -23 ‰ with a minority of coal beds reaching -20 ‰⁵³. The captured CO₂ from the Synfuel plant is thus at the ¹³C-enriched end of the range of likely feedstock isotope values, consistent with our prior discussion.

279

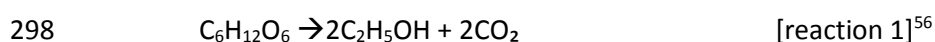
280 **3.3.2 Noble gases:**

281 The noble gas composition of the captured CO₂ stream generated by gasification processes is likely to
282 be controlled by the noble gas content of the feedstock and the steam and oxygen used in the
283 gasification processes. Steam is likely to introduce noble gases that are a mixture of atmosphere and
284 air saturated water (ASW) for the source water. Gasifiers that use partial oxidation rather than steam
285 reforming will likely produce CO₂ enriched in heavy noble gases (Ar, Kr, Xe) from added O₂.

286

287 **3.4 Fermentation**

288 Fermentation of biomass to produce ethanol as a sustainable fuel source is a well-developed industry
289 in the USA and Brazil; while the total anthropogenic CO₂ emissions from bioethanol fermentation
290 make up less than 1% of global CO₂ emissions, the CO₂ gas stream is of high purity and so a suitable
291 target for early adoption of CCS⁷. The two main crops used for bioethanol production are currently
292 corn / maize (USA) and sugarcane (Brazil), both of which are C4 photosynthetic pathway plants⁵⁴.
293 Various other C4 crops, such as miscanthus switchgrass, and C3 plants such as poplar⁵⁵ are under
294 investigation as suitable bioethanol feedstocks due to their ability to grow in relatively arid
295 climates and their lack of economic competition as a food crop⁵⁴. Ethanol is produced from the
296 feedstock by fermentation of the sugars and starches in the biomass, generating a pure stream of CO₂
297 via:



299

300 **3.4.1 Carbon-isotopes:**

301 The carbon isotopic composition of plant sugars generally reflects the bulk plant composition; δ¹³C of
302 glucose from sugar beet (C3) is ~-25.1 ‰⁵⁷ (c.f. -30 to -24 ‰, Table 2) and from maize (C4) is δ¹³C ~-
303 10.5 ‰⁵⁷ (c.f. -15 to -10‰, Table 2). Carbon isotopes are not evenly distributed within the glucose
304 molecules and this results in fractionation of C-isotopes during fermentation^{57,58}; the 3rd and 4th carbon

atoms in the glucose chain are enriched in ^{13}C relative to the bulk sugar, and these form the resulting CO_2 ⁵⁸. Different degrees of ^{13}C enrichment of 3rd and 4th position C-atoms occur between C3 and C4 photosynthetic pathway plants, resulting in hypothetical ^{13}C enrichment of fermentation-produced CO_2 over glucose of $\sim +8.2\text{‰}$ for C3 plants and $+4.5\text{‰}$ for C4 plants⁵⁸. Measured CO_2 -glucose isotope fractionation factors range from $+7.4$ to $+4.6\text{‰}$ for C3 plants and $+5.1\text{‰}$ for C4 plants^{58–60}. Apples are C3 plants and CO_2 produced during fermentation of cider has been measured with $\delta^{13}\text{C}$ of -25 to -21‰ , which is enriched by at least 3‰ relative to C3 plants⁶¹.

Assuming that bioethanol feedstock will be dominated by C4 biomass, and that CO_2 produced by fermentation is enriched in ^{13}C by 4 to 6‰ relative to the original sugars, we can expect CO_2 captured from fermentation plants to have $\delta^{13}\text{C}$ of ~ -11 to -4‰ .

3.4.2 Noble gases:

The main source of noble gases during fermentation will be air saturated water (ASW) in the fermenting solution. Noble gases are more soluble in organic solvents, so we would expect solubility to increase as fermentation proceeds, resulting in noble gas depletion in the CO_2 stream.

3.5 Cement Industry

Cement production (including energy to drive the process and indirect emissions) contributes $\sim 6\%$ of global anthropogenic CO_2 emissions, $\sim 50\%$ of which is from calcination of limestone to produce lime and CO_2 :



The remaining emissions are from the energy required to fire the kiln; coal is commonly used but other fuels, such as natural gas, may be used. Likely carbon capture solutions for the cement industry include oxyfuel combustion to heat the kiln or amine capture for both kiln combustion and calcination gases⁶².

3.5.1 Carbon-isotopes:

Calcination reactions are assumed to not cause isotopic fractionation, so the resulting CO₂ has the same isotopic composition as the initial carbonate^{64,65} – i.e. $\delta^{13}\text{C} \sim 0$. Assuming a 50:50 mixture of CO₂ derived from calcination and from coal combustion we would expect CO₂ emitted from cement factories to have $\delta^{13}\text{C}$ between ~ -11 and -16 ‰.

3.5.2 Noble gases:

As the noble gas content of limestone is low (see supplementary information S.1.5), calcination of limestone is unlikely to significantly contribute noble gases to the CO₂ stream, which will be dominated by noble gases from fossil fuel combustion from firing the kiln.

3.6 Iron and Steel Industry

The steel industry generates 1.9 tonnes of CO₂ per tonne of steel⁶⁶ contributing 4 to 7% of global anthropogenic CO₂ emissions. CO₂ is generated from two processes: energy for steel production by burning of fuel and the use of reducing agents for steel production from iron ore, the most readily available reducing agent being coal⁶⁶. Integrated steel plants (ISP) use mostly coal, with minor natural gas and oil, as both the fuel and reducing agent, while mini-mill plants use electric furnaces to heat and melt scrap or direct-reduced iron (DRI)⁷; while mini-mill plants may not directly produce CO₂ emissions, DRI is produced by reacting iron ore with H₂ and CO to form iron + H₂O + CO₂⁷.

3.6.1 Carbon isotopes:

According to our investigations, there is no published data for carbon isotope fractionation between steel and CO₂, hence estimating $\delta^{13}\text{C}$ of CO₂ produced by integrated steel plants is difficult, but likely to be dominated by combustion CO₂ (so $\delta^{13}\text{C}$ of -31 to -21 ‰). In the case of DRI production an obvious source of H₂ and CO for the reduction process is Syngas. In this case, the $\delta^{13}\text{C}$ of CO₂ resulting from

iron reduction would likely mirror that of the CO, as discussed for Syngas production (i.e. slightly depleted in ^{13}C relative to the gasification feedstock -Section 3.3).

3.6.2 Noble gases:

The overall noble gas budget of CO₂ emitted from steel plants will be dominated by atmospheric noble gases incorporated during combustion, for integrated steel plants, and noble gases introduced during syngas production for mini-mill plants. However, given the low concentration of He in air, enrichment of iron-ore derived radiogenic ^4He may be significant.

3.7 CO₂ separation

3.7.1 Chemical absorption

Chemical absorption involves passing flue gases through a solvent with a high affinity for CO₂ (most commonly an amine solvent). In a typical amine capture process a CO₂-bearing flue gas is reacted with the amine solvent at ~ 40 to 60 °C and the remaining flue gas (which will contain some residual CO₂) cleaned and vented; the CO₂-bearing solvent is transferred to a desorber vessel and heated to 100-140 °C to reverse the CO₂-binding chemical reaction and release a stream of pure (>99%) CO₂ gas^{7,67}. Typical CO₂ recoveries are 80% to 95% of the CO₂ in the flue gas⁷. Such techniques are commonly employed to remove CO₂ from natural gas, before it is piped to national gas grids⁷. Various capture plants and aqueous amine solvents are being developed for chemical absorption of CO₂. The effects on inherent tracer composition will likely depend on the relative efficiencies of the absorption / desorption processes used by the capture process, the specific chemical reaction pathways that occur and the temperature and pH of the reactions. Two reaction pathways are common for amine solvents: bicarbonate (HCO_3^-) and carbamate (NH_2CO_2^-) formation⁶⁷.

Carbon-isotopes:

No data is yet available for C-isotope fractionation in the amine solutions commonly used in CO₂ capture. For water, C-isotope fractionation between CO₂ gas and bicarbonate is greater at lower temperatures²⁷. In terms of carbon capture, this suggests that greater isotopic fractionation will take place during the absorption stage than the desorption stage. Below, we use Rayleigh Fractionation²⁷ to calculate expected $\delta^{13}\text{C}$ values for absorbed and desorbed CO₂.

In water at typical amine absorption temperatures (40-60 °C), the bicarbonate-CO₂ enrichment factor will be between +4 to +7 ‰^{27,68}. If 85-99% of the CO₂ dissolves to form bicarbonate in the amine solution, the resulting bicarbonate will be enriched in ¹³C by 0 to +2.34 ‰ relative to the original CO₂ flue gas. At desorption temperatures (100-140 °C), the HCO₃⁻ - CO₂ enrichment factor will be ± 1 ‰⁶⁸, and if 99% of the bicarbonate is desorbed, the resulting CO₂ will have a $\delta^{13}\text{C}$ value between -0.06 and +0.06 ‰ compared to that of the saturated bicarbonate. The net enrichment of captured CO₂ relative to original flue CO₂ will therefore be between -0.06 and +2.4 ‰, depending on the absorption and desorption temperatures.

An isotope fractionation factor of +1.011 (equivalent to an enrichment factor of $\sim +11$ ‰) has been determined for carbamate relative to aqueous CO₂⁶⁹. ¹³C enrichment between gaseous and aqueous CO₂ in fresh water at typical amine absorption temperatures (40-60 °C) is -0.9 to -1.0 ‰²⁷ and so the net isotope enrichment factor of carbamate relative to the original CO₂ flue gas will be $\sim +10$ ‰. If 85-99% of the CO₂ dissolves to form carbamate in the amine solution, the resulting carbamate will be enriched in ¹³C by +0.5 to +3 ‰ relative to the original flue gas CO₂. If 99% of the carbamate is desorbed, the resulting CO₂ will have $\delta^{13}\text{C} \sim 0.5$ ‰ lower than the saturated carbamate, resulting in a net enrichment of ¹³C in the captured CO₂ of 0 to +2.5 ‰ relative to the original flue gas.

The anticipated ¹³C enrichment in CO₂ from amine capture, relative to the original flue gas CO₂, will be between -0.06 and +2.5 ‰, with the exact enrichment value dependant on absorption and desorption

temperature, and the relative proportions of bicarbonate and carbamate species in the amine solution.

However, work investigating C-isotope fractionation during absorption of CO₂ by NH₃-NH₄Cl solutions at room temperature suggests that, in alkaline solutions, dissolved carbon (bicarbonate and carbamate ions) may be depleted in ¹³C relative to the CO₂ gas by more than -50 ‰⁷⁰. In the context of the above discussion regarding absorption / desorption efficiency, this may result in significant ¹³C depletion in the captured CO₂ relative to the source gas, the opposite effect of what would be expected from dissolution in water.

The CO₂ injected at the Pembina CCS project was derived from the Ferus natural gas processing plant⁷¹, which presumably used a form of chemical absorption to strip CO₂ from natural gas. It had δ¹³C ~ -4.7‰¹¹, which falls well within the range of values for CO₂ co-existing with natural gas (-13.9 to +13.5⁷², Fig. 1). Similarly, CO₂ captured using amine solvents from steam reforming of methane (see gasification, above) has δ¹³C of -37 ‰^{49,51}, well within the isotopic range of natural gas (-20 to -52 ‰). Given the breadth of possible δ¹³C values for the source CO₂, these data do not help to constrain which of the above hypotheses is true, but suggest that ¹³C enrichment of the captured CO₂ relative to the original CO₂ is less than ± 20 ‰. More work to experimentally determine C-isotope fractionation during CO₂ capture would be beneficial. In the meantime, we tentatively conclude that fractionation of C-isotopes during amine capture is likely between -20 ‰ and +2.5 ‰ relative to the source CO₂, based on the available data for captured CO₂ relative to feedstocks, and the likely maximum enrichment calculated for CO₂ dissolution in fresh water.

Noble gases:

Little data is available for the noble gas content of the CO₂ stream produced by chemical absorption. In a summary of the CO₂ product stream specifications from a number of post-combustion capture

technologies⁷³, Ar was present at concentrations of 10-25 ppmv, much lower than the atmospheric concentration of 9340 ppmv (Table 1). This is likely due to the unreactive noble gases remaining in the gas phase during absorption and subsequently being vented, rather than being absorbed with the CO₂. A small proportion of the noble gases will dissolve into the amine solution. As noble gas solubility decreases with increasing temperature, these will be efficiently exsolved when the solvent is heated to release the CO₂. Noble gas solubility is controlled by Henry's Law with the heavy noble gases having greater solubilities than lighter noble gases. As a result we might expect noble gas element ratios to show heavy element enrichment relative to atmosphere.

3.7.2 Physical absorption

Physical absorption of CO₂ requires a high partial pressure of CO₂ and is often used to separate CO₂ from other gases in CO₂-rich gas streams, such as the products of gasification processes. CO₂ absorption or dissolution into the solvent is according to Henry's Law⁷⁴. No chemical reaction takes place and the absorbed gas is released from the solvent by pressure reduction. Physical absorption using cold methanol is used to capture CO₂ produced at the Great Plains Synfuel plant, North Dakota, USA, for use in the Weyburn enhanced oil recovery (EOR) and CCS site⁷.

Carbon isotopes:

To the best of our knowledge there is no data available to assess the effect of physical absorption on $\delta^{13}\text{C}$ -CO₂. However, we would expect an enrichment of ¹³C in the dense phase²⁷ (i.e. dissolved in the solvent) and the isotopic composition of the resulting captured CO₂ will depend on the relative efficiencies of the absorption and desorption mechanisms. If desorption is more efficient than absorption, then a small degree of ¹³C enrichment is likely.

Noble gases:

In general, noble gases have a much higher solubility in organic solutions than in water^{75,76} and follow Henry's Law, with the heavier noble gases having higher solubility. However, as is the case with noble gas dissolution in amine solvents, the noble gases will be preferentially retained in the gas phase and become decoupled from the CO₂. The small proportion of noble gases that are absorbed into the solvent will likely be enriched in the heavier noble gases relative to atmosphere due to the enhanced solubility of the heavier noble gases. Assuming efficient desorbing of gases from the physical solvent, CO₂ captured via physical absorption is likely to contain low concentrations of noble gases with element ratios enriched in heavy noble gases relative to the noble gas composition of the original flue gas. Isotopic ratios, however, are unlikely to change.

4. Geochemistry of fluids and gases in actual and potential CCS storage sites

The two types of storage sites currently considered to have the most potential for CCS in the short term are depleted oil and gas fields, and deep, saline formations. In geological terms, these two types of storage are very similar, comprising reservoir rocks filled with saline fluid. In the case of depleted hydrocarbon fields, a wealth of information is available from hydrocarbon exploration and the fields are proven to have stored buoyant fluids or gas over geological timescales. On the other hand, many wells may have been drilled in such fields, resulting in potential leakage pathways and many hydrocarbon fields are too small to provide large-scale CO₂ storage. Conversely, saline aquifers are much larger, but are poorly studied due to lack of hydrocarbon accumulation and it is not conclusively known whether a given aquifer is leak-tight with respect to buoyant fluids. Porous basalt formations pose another promising storage option⁷⁷ but the chemical and transport processes involved in these cases have significant differences compared to storage in sedimentary formations, and are beyond the scope of this review.

To trace CO₂ injected into a storage reservoir, the baseline conditions of the reservoir, and the likely in-reservoir processes need to be known. Hydrodynamically closed reservoirs will tend to have more

stable baseline conditions and predictable behaviour, while hydrodynamically open reservoirs, and depleted hydrocarbon reservoirs that, at best will be contaminated with drilling fluids and at worst may have been flushed with water to aid hydrocarbon recovery, may have spatially and temporally variable baselines and thus exhibit less predictable behaviour. Below we summarise the measured and expected geochemical baselines for potential storage reservoirs. While a reasonable amount of data is available for hydrocarbon reservoirs, less information is available for the baseline evolution after production ceases. Data for non-hydrocarbon bearing saline aquifers are uncommon.

4.1 Carbon-isotopes:

The $\delta^{13}\text{C}$ of CO_2 in storage formations generally varies between ~ -23 and $+1$ ‰ (Figure 2, Supplementary Table S3). Formations that experience rapid flow of formation water, or mixing of water reservoirs may exhibit a large range in $\delta^{13}\text{C}_{\text{CO}_2}$ values at a single site (e.g. -23 to -16 ‰ at Weyburn⁷⁸). $\delta^{13}\text{C}$ for DIC are more constrained, based on the available data, and fall between -9 and $+3$ ‰ (see supplementary Table S3), regardless of whether the host rock is carbonate or siliciclastic, or whether the storage formation has experienced previous hydrocarbon exploitation, but this may reflect a limited dataset. For storage reservoirs in depleted hydrocarbon fields or associated with EOR, the baseline isotope values may fluctuate strongly depending on industrial activities, such as water flushing⁷⁹ or contamination with organic matter resulting in enhanced bacterial action⁸⁰.

4.2 Noble gases:

The most comprehensive noble gas measurements from a CCS reservoir are from the Weyburn EOR project⁸¹, although these do not represent baseline data. ^4He concentrations were 2 orders of magnitude greater than for air saturated water (ASW) while other noble gas isotopes (Ne – Kr) had concentrations 1-2 orders of magnitude lower. The isotopic composition of the noble gases is consistent with a depletion in atmospheric noble gases, as would be expected for a hydrocarbon-rich formation where the noble gases partition into the hydrocarbon phase, rather than the pore-water

phase, and an enrichment in radiogenic isotopes, consistent with a deep-origin of the fluid. Similarly at the Cranfield CO₂-EOR site, noble gas data from produced gases indicate high levels of terrigenous / radiogenic ⁴He in the reservoir⁸². Other noble gas data are available for fluids from the Rousse and Frio storage reservoirs. The Frio data are restricted to He and Ar concentrations (80,000 ppb (>> air) and 400,000 ppb (≈ ASW) respectively⁴⁸). Air-normalised concentrations for ⁴He, ²⁰Ne, ³⁶Ar, ⁴⁰Ar and ⁸⁴Kr, from Rousse show that, while the concentration of ⁴He was ~ ten times greater than air, the remaining noble gases were all 100 to 1000 times lower than air, with a positive correlation between concentration and elemental mass³⁷.

These observations are consistent with the formation waters having interacted with hydrocarbons, causing depletion in atmospheric noble gases (originally derived via hydrologic recharge) relative to expected air saturated water (ASW), due to preferential partitioning into the hydrocarbon phase (Section 2.2). Repeated dissolution and exsolution of noble gases will produce greater degrees of elemental fractionation, with an enrichment of heavy relative to light noble gases, compared to air⁸³. While these processes facilitate precise quantitative modelling when all of the relevant conditions are well characterised, it is difficult to place more quantitative constraints on the range of noble gas concentrations that could be expected in deep aquifers.

The isotopic composition of subsurface noble gas elements, however, does not fractionate during dissolution and exsolution and is instead controlled by mixing between different sources of noble gases. In very simplistic terms, the formations likely to be of most interest for CCS are those that have at least some degree of hydrodynamic isolation. In such cases, the fluids in the reservoir will be relatively old, residing in the subsurface for a considerable amount of time, perhaps approaching geological timescales. This will give a much stronger radiogenic and terrigenous noble gas signature than would be observed for shallow, freshwater aquifers that undergo regular recharge (see Section 7). Noble gases in hydrocarbon systems often have a resolvable mantle component identified by elevated

³He, and a high proportion of radiogenic isotopes that are often correlated with reservoir depth (⁴He*, ²¹Ne*, ⁴⁰Ar*, with “*” denoting a radiogenic origin)^{30,84–86}. Some hydrocarbon fields have elevated, isotopically atmospheric, Kr and Xe that cannot be explained by elemental fractionation in a water-oil-gas system. This is attributed to adsorption of atmospheric Kr and Xe onto the carbon-rich sediments that are the source of hydrocarbons^{30,87}. Such sediment-derived Kr and Xe enrichments may occur in hydrocarbon fields, but would partition into the hydrocarbon phases, rather than water and so are unlikely to be observed in saline aquifers or depleted hydrocarbon fields where the Kr and Xe enriched phase was either never present or has been removed.

In the case of depleted oil and gas fields an additional source of noble gases may be introduced during water-stimulation to maintain reservoir pressure. The extent of this contamination will depend on the relative volumes of water added, amount of original formation water remaining, and the noble gas composition of the injected water. If sea water is injected, as is likely in offshore hydrocarbon fields, the added noble gases will be those of atmosphere equilibrated sea water (similar order of magnitude concentrations to those quoted for fresh water in Table 1). If produced fluids from the field are simply reinjected, then the noble gas composition is unlikely to change.

Many factors control the noble gas composition of potential storage reservoirs and so good noble gas baseline data will be beneficial if noble gases are to be used as tracers. Many reservoirs are likely to have elevated He concentrations relative to air or ASW and be depleted in other noble gases, while isotopic ratios will show strong radiogenic and terrigenous components. Saline aquifers will likely have more stable and consistent baselines than depleted hydrocarbon fields where contamination from production processes is likely.

5 Geochemical evolution of the CO₂ stream on injection and migration in the subsurface

Once injected into a geological storage formation, the fingerprint of the CO₂ stream will change depending on the processes and reactions that take place and the timescale and rate of those reactions. This section describes the changes that are likely to take place as the CO₂ plume migrates through the subsurface. Dominant processes will be mixing of the injected CO₂ with pre-existing materials, dissolution of the injected CO₂ into formation waters, fluid-rock reactions such as dissolution of carbonate minerals, and migration. Precipitation of secondary carbonate and clay minerals will also change the stable isotope composition of the carbon-bearing gases and fluids in the subsurface, but there is currently limited evidence that these processes will occur on site-monitoring timescales and, given the current uncertainties regarding mineral precipitation during CO₂ storage, these will not be considered here. Transport of CO₂ through the subsurface can be considered in terms of diffusive and advective transport, both of which may affect the composition of the CO₂ plume in different ways.

5.1 Carbon isotopes

δ¹³C evolution of injected CO₂ has been covered by a number of recent review papers^{11,12,19,23–26} and so is only qualitatively described here. Injected CO₂ will first mix with any free-phase CO₂ in the reservoir, resulting in a CO₂ plume with a δ¹³C value resulting from mixing between injected and baseline values. Identification of the injected CO₂ plume is thus dependent on the difference between the injected and baseline δ¹³C_{CO₂}, the relative volumes of injected and baseline CO₂, and relevant enrichment factors (which in turn are dependent on temperature and salinity) between gases and dissolved C-species

CO₂ will begin to dissolve into the formation water to form dissolved inorganic carbon (DIC), with isotopic fractionation between CO₂ and DIC related to temperature, pH and the DIC species formed. At reservoir conditions, DIC derived from the injected CO₂ is calculated to be enriched in ¹³C by -1 to +7 ‰ relative to the co-existing CO₂²⁷. This DIC will subsequently mix with baseline DIC.

Carbonic acid formation may cause dissolution of any carbonate minerals present, adding another source of C to the DIC; the stable isotope composition of these carbonate minerals, and thus resulting $\delta^{13}\text{C}_{\text{DIC}}$ depends on the origin of the carbonate (Figure 1).

Diffusive transport through rock or soil pore networks may cause C-isotope fractionation at the migration front, resulting in sequential ^{13}C depletion and then enrichment at a given location as the migration front passes^{12,88}. For dry systems, if reactive mineral surfaces such as illite are present, $^{44}[\text{CO}_2] (^{12}\text{C}^{16}\text{O}_2)$ may be preferentially adsorbed onto the surfaces, resulting in an initial ^{13}C enrichment of the free-phase CO_2 , that can change the $\delta^{13}\text{C}_{\text{CO}_2}$ by up to hundreds of permil, followed by ^{12}C enrichment relative to the bulk CO_2 as the $^{12}\text{CO}_2$ is desorbed, resulting in lower $\delta^{13}\text{C}$ values, before returning to the bulk composition⁸⁹. Further work is needed to investigate the presence of this effect in fluid saturated systems. While these processes are unlikely to affect the bulk of CO_2 injected for storage, they may affect the migration front of the injection plume and any CO_2 that leaks from the storage site. Early measurements of $\delta^{13}\text{C}_{\text{DIC}}$ at the Ketzin observation well Ktzi 200 gave $\delta^{13}\text{C}$ values lower than expected for mixing of CO_2 sources and calculated C- isotope fractionation during dissolution; diffusive fractionation was a speculated cause of this depletion⁸⁰.

5.2 Noble gases

The processes affecting noble gases in the subsurface are described in a number of recent summary papers and text books^{28–30,90,91}. As with stable isotopes, the noble gas signature of the injected CO_2 stream will first be modified by mixing with any atmospheric, terrigenic and radiogenic noble gas components in the reservoir gas phase. Exchange of noble gases between different reservoir phases (gas, water, oil, solid particles) may take place according to the differences in solubility described in Section 2.2. Note from Table 1 that Xe will partition preferentially into oil rather than gas at temperatures less than 50 °C and so interaction of the injected CO_2 with any oil in the subsurface will

cause Xe depletion in the gas phase. Recent work⁹² experimentally determined noble gas partitioning between supercritical CO₂ and water and found deviations relative to ideal gas – water partitioning behaviour that became greater with increasing CO₂ density. Ar, Kr and Xe all show an increasing affinity for the CO₂ phase with increasing CO₂ density, due to enhanced molecular interactions of denser-phase CO₂ with the larger, more polarisable noble gases, while He shows decreasing affinity⁹².

Physical adsorption of noble gases onto solid particles, while difficult to quantify due to a lack of experimental data on adsorption properties, may significantly fractionate heavy from light noble gas elements and a number of studies indicate enrichment of Kr and Xe in organic rich shales and coal^{29,93,94}

Migration of the plume-front may chromatographically fractionate the noble gas elements and CO₂ due to differences in molecular diffusion rate and solubility, although the specific manifestation of this fractionation depends on the rock matrix, the gas transportation mechanism and relative solubility of the gas species. Less soluble species will migrate faster than more soluble species⁹⁵, meaning that noble gases, which will preferentially partition into the gas phase, should travel faster through the subsurface than CO₂, which will begin to dissolve on contact with water. If gas transport takes place via molecular diffusion through pore space, the lighter, faster diffusing species will travel more quickly through the subsurface than the heavier, slower diffusing species. In the case of arrival of the migration front at a monitoring well, we would expect to detect gases in the following order, with the delay between gas arrival dependant on the distance travelled: He, Ne, Ar, CO₂, Kr, Xe⁹⁶. However, the opposite may be true when gas transport is via advection along fractures, with faster-diffusing species, which are more able to enter the rock pore-space, travelling less rapidly than slower diffusing species, which are confined to fractures and more open, faster flow pathways⁹⁷. The isotopic composition of the noble gases, however, is not expected to be altered by migration, and so characterisation of

baseline and injected noble gas isotope compositions will allow mass-balance modelling and fingerprinting of any subsurface samples produced from monitoring wells.

6. Past and present use and future potential of inherent tracers for in-reservoir processes in CCS projects

A number of projects have successfully used inherent stable isotopes to monitor CO₂ behaviour in the subsurface, while added noble gases have also proven useful. Supplementary Table S4 summarises the ways that these tracers have been used in different CCS projects and identifies the key papers describing these applications. Many of these projects and applications have been summarised in recent review papers^{12,17,26}.

Using C-isotopes as a CO₂ or DIC fingerprint to detect breakthrough and monitor migration of the injected CO₂ is the most common application of inherent tracers in existing CCS projects. In most of these projects the injected CO₂ was isotopically distinct from baseline CO₂ and DIC. However C-isotopes were still a useful tool for monitoring migration and breakthrough at Weyburn, where the injected and baseline $\delta^{13}\text{C}_{\text{CO}_2}$ overlap (due to the wide range of baseline values), and at Pembina, where the injected $\delta^{13}\text{C}_{\text{CO}_2}$ overlapped with baseline $\delta^{13}\text{C}_{\text{DIC}}$ (Figure 2). In these cases, C-isotope fractionation during dissolution of injected CO₂ to form bicarbonate (~ 5 ‰ at 50-60 °C) increases the separation in $\delta^{13}\text{C}$ values between baseline DIC and injection-derived derived HCO₃⁻. In many cases (see Supplementary Data Table S4), C-isotopes were the most sensitive tracer, indicating arrival of injected CO₂ at a monitoring well earlier than significant changes in fluid pH or CO₂ concentration. When the baseline conditions are well characterised, C-isotopes have proven to be useful for quantifying the proportion of CO₂ or DIC derived from the injected CO₂ and from in-reservoir mineral dissolution (Weyburn^{12,98–100}, Cranfield¹⁰¹ and Ketzin⁸⁰). C-isotopes have also proven useful at identifying contamination from drilling fluids⁸⁰.

Hence, $\delta^{13}\text{C}$ of CO_2 and DIC has the potential to be a powerful in-reservoir tracer, as long as the injected CO_2 has a $\delta^{13}\text{C}$ value that is easily distinguishable from background CO_2 and, if it dissolves, will produce DIC with $\delta^{13}\text{C}$ distinguishable from baseline DIC. Figure 3 compares the expected $\delta^{13}\text{C}$ of captured CO_2 from a number of processes and feedstocks, to the range of likely baseline storage formation values. From this, we can see that C3 biomass and fossil fuel derived CO_2 will be easiest to distinguish from reservoir baseline conditions, using $\delta^{13}\text{C}$, although coal and C3 biomass derived CO_2 have a greater chance of overlap.

While no studies have taken place using noble gases inherent to captured CO_2 as a tracer, use of noble gases co-existing with natural CO_2 injected for EOR operations³¹ and as added tracers for both tracing CO_2 migration (Frio, Ketzin) and quantifying residual saturation (Otway) suggest that noble gases could prove very useful, if their injected composition is different to those of the reservoir baseline. In addition to experimental CCS sites, natural tracers have been used to study reservoir processes in natural CO_2 accumulations with combined noble gas and C-isotope measurements identifying CO_2 dissolution into the formation waters¹⁰².

7. Geochemistry of potential leakage reservoirs (atmosphere, soil and groundwater aquifers)

The aim of CCS is to prevent CO_2 from entering the atmosphere and so being able to detect seepage of geologically stored CO_2 to the atmosphere is a high priority. However, this remains difficult due to problems associated with identification of leakage sites, leakage plume dilution, and difficulties in establishing a precise local atmospheric baseline. In this section we will briefly review the probable range of baseline conditions for C-isotopes and noble gases in the reservoirs most likely to be influenced by CO_2 leakage and how these may or may not contrast with CO_2 leakage signatures.

7.1 Atmosphere

C-isotopes

Atmospheric CO₂ has $\delta^{13}\text{C}$ of between -6 and -8 ‰ V-PDB²⁷ (Figure 1), but may vary spatially and temporally with local conditions, weather, and anthropogenic activity; e.g. atmospheric measurements in Dallas, Texas, ranged from $\delta^{13}\text{C}_{\text{CO}_2}$ of -12 to -8 ‰ over ~ 1.5 years due to varying photosynthetic uptake, respiration and anthropogenic sources (vehicle emissions)¹⁰³. C-isotopes can be a sensitive tracer, despite large background fluctuations, by using Keeling plots, which correlate $\delta^{13}\text{C}_{\text{CO}_2}$ with inverse CO₂ concentration to determine the isotopic composition of local CO₂ (ecosystem respired and anthropogenic sources) mixing with regional atmospheric CO₂¹⁰⁴. If injected CO₂ were to leak to the atmosphere from the subsurface, it should be identifiable using Keeling plots as long as its $\delta^{13}\text{C}$ is different to that of the (previously established) baseline end members. Keeling plots from North and South America suggest that ecosystem respired CO₂ has $\delta^{13}\text{C}$ between -33 and -19 ‰¹⁰⁴, which is similar to the anticipated $\delta^{13}\text{C}$ of CO₂ captured from burning C3 biomass and some fossil fuels; $\delta^{13}\text{C}$ of captured CO₂ may thus be especially difficult to distinguish from surface CO₂. Captured CO₂ derived from natural gas combustion may be depleted enough in ¹³C and CO₂ captured from natural gas processing plants may be sufficiently enriched in ¹³C to be distinguishable from local and regional atmospheric sources of $\delta^{13}\text{C}$.

Noble gases:

The concentration of noble gases in the atmosphere is given in Table 1. Atmospheric values for commonly used noble gas isotopic ratios include: $^3\text{He}/^4\text{He} = 1 \text{ R/R}_\text{A}$ ¹⁰⁵; $^{20}\text{Ne}/^{22}\text{Ne} = 9.8$ ¹⁰⁵; $^{40}\text{Ar}/^{36}\text{Ar}=298.56$ ¹⁰⁶. Regardless of the inherent noble gas composition of the injected CO₂ stream, if CO₂ leaks from deep geological storage it will most likely be accompanied by baseline reservoir noble gases, which will be enriched in radiogenic and terrigenous isotopes (e.g. $^3\text{He}/^4\text{He} \ll 1 \text{ R/R}_\text{A}$; $^{40}\text{Ar}/^{36}\text{Ar} > 298.56$).

7.2 Soil

C-isotopes

As with atmosphere, the stable isotope composition of soil CO₂ can vary spatially and temporally with local conditions. It is governed by a combination of CO₂ produced by soil respiration, fractionation during diffusion, mixing with atmospheric CO₂ and by isotopic exchange with soil water^{88,107}. This can result in highly variable δ¹³C values for soil that vary on a daily basis. δ¹³C data are available for soil from a number of CCS sites (Supplementary Table S5), all of which show more than 10 ‰ variation (between -27 and -7 ‰) with no evidence of being contaminated by injected CO₂. There is considerable overlap between the δ¹³C of soil CO₂ and the expected range of δ¹³C values of captured CO₂ (Figure 3). CO₂ derived from combustion or gasification of natural gas may produce CO₂ significantly more depleted in ¹³C than soil CO₂, while CO₂ captured from natural gas processing may be significantly enriched. Given the wide variation in baseline soil δ¹³C values at any given site, C-isotopes in isolation will only be a useful leakage tracer if the leaking CO₂ has a distinctive δ¹³C (i.e. derived from natural gas or natural gas processing), and if CO₂ concentration is also measured and Keeling Plots are used. Use of δ¹³C_{CO₂} in conjunction with concentrations of oxygen and nitrogen can be a useful tool to identify mixing between atmospheric CO₂ and CO₂ produced in the soil from biological respiration or methane oxidation¹⁰⁸.

Noble gases

In simplistic terms, noble gases in soil are derived from the atmosphere and partition between gas and water phases; soil gas should have an atmospheric noble gas composition, while fluids have concentrations consistent with air saturated water (ASW) for the local soil temperature¹⁰⁹. However, this ideal theoretical behaviour is not always observed. Changes to the local combined partial pressure of CO₂ and O₂ (due to the greater solubility of CO₂ over O₂) can cause corresponding changes to noble gas concentrations and elemental ratios, with heavier noble gases more affected than lighter noble gases, likely due to differences in diffusion rate⁹⁰, though isotopic ratios remain atmospheric. Three soil gas monitoring projects associated with CCS sites provide limited noble gas concentration data (Supplementary Table S5). At Weyburn, Ar concentrations¹¹⁰ are atmospheric (~0.9%) and at Rouse,

He concentrations from four separate campaigns were consistent at $\sim 5 \text{ ppm}^{111}$, again consistent with atmospheric concentrations. At Otway, baseline He concentrations in the soil ranged from 3 to 103 $\text{ppm}^{112,113}$ i.e. ranging between enriched and slightly depleted compared to atmosphere. The reasons for these elevated He concentrations were unknown, but not thought to represent leakage of a deep gas source.

In terms of using noble gases to detect leaking CO_2 , isotopic ratios will be the most useful tool. The isotopic ratios of noble gases in baseline soil will be atmospheric (see above), while noble gases in CO_2 leaking from depth will most likely have $^3\text{He}/^4\text{He}$ below atmospheric values, and $^{40}\text{Ar}/^{36}\text{Ar}$ greater than atmosphere, irrespective of the noble gas composition of the injected CO_2 , due to enrichment of radiogenic $^4\text{He}^*$ and $^{40}\text{Ar}^*$ in the subsurface (see Sections 2.2 and 4). Concentrations of noble gas elements or isotopes may provide additional information, depending on the noble gas content of the injected CO_2 , and as long as variations in baseline soil noble gas partial pressure and elemental fractionation due to changing $\text{CO}_2 + \text{O}_2$ content are taken into account.

7.3 Shallow aquifers

Shallow aquifers are often sources of potable water and hence CO_2 leakage into such reservoirs is undesirable. Such reservoirs are recharged by meteoric water, are thus hydrodynamically connected to the surface and so leakage of CO_2 into a shallow aquifer will likely result in escape of some of that CO_2 to the atmosphere. For these reasons, identification and mitigation of any CO_2 leakage into shallow aquifers will be a high priority.

Compared to the atmosphere or soil, baseline geochemical conditions in aquifers are likely to be much more stable, thus providing a higher sensitivity for leak detection. Furthermore, if the hydrodynamic gradient of an aquifer is well characterised, monitoring wells can be placed downstream of any

potential leakage structures, allowing efficient monitoring of a relatively large area without the need to identify and monitor every single potential leakage point¹¹⁴.

C-isotopes

The $\delta^{13}\text{C}$ value of CO_2 and DIC in fresh spring and groundwaters is generally derived during recharge from the soil, followed by dissolution, associated isotope fractionation (see Section 5) and weathering of carbonate material²⁷. Bacterial action can isotopically enrich DIC in ^{13}C (up to +30 ‰), via reduction of CO_2 to methane (Figure 1), or fermentation of acetate to produce CH_4 and CO_2 ^{115–118}.

Supplementary Table S5 lists $\delta^{13}\text{C}$ for CO_2 and DIC in selected freshwater springs and aquifers. Data for Ketzin, Altmark, Otway and Hontomín were collected as part of CCS monitoring programmes. $\delta^{13}\text{C}$ values of both CO_2 and DIC range from -24 to -9 ‰, consistent with derivation from soil CO_2 (Figure 1). Data from other aquifers extend the range to higher values, indicating bacterial action. $\delta^{13}\text{C}$ of CO_2 in shallow aquifers may be difficult to distinguish from $\delta^{13}\text{C}_{\text{CO}_2}$ of captured and injected CO_2 , especially that derived from coal and biomass feedstocks and cement manufacture.

Noble gases

Noble gases enter subsurface aquifers via recharge of meteoric water in the vadose zone of soils and baseline compositions reflect air saturated water (ASW), with or without excess air, for the local soil temperature¹⁰⁹. While deviations from this ideal behaviour have been noted, these are most likely explained by changes to noble gas partial pressure in soil, described above⁹⁰. In general, the processes that result in noble gas elemental fractionation in meteoric and groundwater are controlled by well understood physical mechanisms, are related to the residence time of water in the subsurface, and can be modelled³². Groundwater may thus provide a well constrained, predictable baseline for leakage monitoring using noble gases. Furthermore, as noble gases are sparingly soluble in water, the concentration of noble gases in ASW is significantly lower than that of the atmosphere, resulting in a

signal to noise ratio that is 100 times more sensitive¹¹⁹. While the processes controlling the noble gas content of groundwater are well understood and their behaviour predictable, they are dependent on specific local recharge conditions, and so establishing a precise baseline is essential. As with atmospheric and soil reservoirs, the baseline of recently recharged aquifers is likely to differ from leaking CO₂ by a lack of radiogenic and terrigenous noble gases. However, old (hundreds of thousands of years) groundwaters may exist in aquifers used as domestic and agricultural water sources, and such aquifers may have significant radiogenic and terrigenous components. One such example is the Milk River aquifer in Alberta, Canada, which has groundwater residence times of up to 500 ka¹²⁰. The majority of noble gases have concentrations between 0.2 and 4 times the expected values for ASW, but radiogenic and terrigenous-derived ⁴He is enriched in some wells by more than 2000 times the expected ASW value and ⁴⁰Ar/³⁶Ar values are all greater than atmosphere¹²¹.

8. Past and present use and future potential of inherent tracers for leak detection in CCS projects

Use of tracers for monitoring leakage of CO₂ into overlying reservoirs (aquifers, soil, atmosphere) follows the same principles as for in-reservoir monitoring, but with the added complication that the released volumes are likely to be much smaller and so sensitivity and detection become a critical issue. Geochemical analysis is a common monitoring technique for CCS sites, many of which employ surface, soil and / or groundwater analysis to monitor for leakage or contamination and a recent review¹⁹ provides more details on the theory and practice of using tracers to detect CO₂ leakage into freshwater aquifers. However, in the vast majority of CCS field tests, no leakage has been observed and these projects are thus of limited value in assessing the viability of using inherent tracers as leakage detection. An exception is the Frio CCS project, where added tracers, elevated dissolved CO₂ gas contents, slight increases in HCO₃⁻ concentrations and substantial depletion in ¹³C of DIC were found in strata above a primary seal (but remaining below the main structural trap for the storage reservoir), indicating that CO₂ had leaked within the subsurface⁴⁸. These indicators returned to background levels within nine months of injection, suggesting that the leak was short-lived and occurred early in the

injection process. Given that the injection well was 50 years old, leakage from the well itself was considered to be the most likely source of the CO₂, rather than migration between strata⁴⁸. While it was not possible to calculate the volumes of leaked CO₂ at Frio, it seems that C-isotopes of DIC may provide a potentially powerful tracer of CO₂ leakage when volumes are so low that there is no significant rise in HCO₃⁻ concentration.

At the Rangely-Weber CO₂-EOR site, Colorado, CO₂ and CH₄ gas fluxes were used to quantify micro-seepage from the reservoir¹²². Statistical analysis showed that gas flux and isotopic composition was different between the area overlying the reservoir, and a nearby control site, but it was not possible to conclusively attribute these differences to gas seepage from the reservoir. Assuming that the differences were due to gas seepage, maximum seepage rates of 170 tonnes per year CO₂ and 400 tonnes per year CH₄ were calculated¹²².

Allegations of CO₂ leakage from the Weyburn EOR site into farmland (the Kerr Property) were shown to be unfounded¹²³, but this case study provides useful insights of how natural tracers can help to determine the origin of CO₂, even when robust baseline data is not available. A number of incidents and CO₂ measurements led the owners of the farmland to believe that CO₂ injected into the Weyburn site was leaking into their property. One of the reasons for this belief highlights a potential downfall of using stable isotope data for tracing CO₂ migration; high concentrations of CO₂ measured in the soil had the same δ¹³C_{CO₂} as the CO₂ being injected as part of the Weyburn project. This δ¹³C_{CO₂} value (~ -21 ‰) was, however, comparable to typical soil gas CO₂ compositions¹²⁴ (c.f. Figure 1). An independent investigation was commissioned to determine the origin of CO₂ on the site, the results of which showed without doubt that the CO₂ was natural and did not derive from injection of CO₂ for storage or EOR at Weyburn¹²⁴. For soil gas, correlations of CO₂ with O₂ and N₂ were consistent with a CO₂ origin by soil respiration, rather than addition of an extra CO₂ component, and correlating CO₂ concentration with δ¹³C_{CO₂} showed that the soil gas isotope composition was easily explained by

845 mixing between atmospheric CO₂ and soil gas CO₂ with a $\delta^{13}\text{C}_{\text{CO}_2}$ of -25 ‰¹²⁴. Noble gas and C-isotope
846 analyses on groundwater well samples, injected CO₂ and water and fluids produced from deep in the
847 Weyburn formation confirmed that gas from the reservoir was not present⁸¹. Noble gas
848 concentrations in the shallow groundwaters were consistent with air-saturated water (ASW), as would
849 be expected for the local groundwater system, while the fluids produced from the Weyburn field were
850 very different; most noble gas concentrations (Ne, Ar, Kr, Xe) in the Weyburn fluids were much lower
851 than would be expected for ASW, while ⁴He concentrations were much higher, consistent with
852 enrichment of radiogenic ⁴He in the crust⁸¹. Furthermore, ³He/⁴He ratios in groundwater samples were
853 indistinguishable from air, while Weyburn fluids had ³He/⁴He values an order of magnitude lower, due
854 to addition of crustal radiogenic ⁴He⁸¹. Importantly, Weyburn reservoir water and shallow
855 groundwater samples showed no correlation on a plot of HCO₃⁻ vs ³He/⁴He, which would be expected
856 if mixing occurred between deep, Weyburn fluids and ASW groundwater⁸¹.

857
858 In the absence of real CO₂ leaks from storage sites, information on tracer behaviour during leakage
859 can only be gleaned from controlled release experiments (i.e. injecting CO₂ into a unit that will leak)
860 and studying natural CO₂ or natural gas seeps. Experiments releasing CO₂ into soil at a rate comparable
861 to 0.001% leakage from a 200 Mt CO₂ storage site have been successful at identifying CO₂ leakage
862 using $\delta^{13}\text{C}$ with Keeling plots in both atmosphere and soil, although in these cases the injected CO₂
863 had a particularly light isotopic signature ($\delta^{13}\text{C} < -45$ ‰)^{35,125–127}. An experimental CO₂ leak ($\delta^{13}\text{C}_{\text{CO}_2}$ -
864 26.6 ‰) into sediments in the North Sea (QICS project) showed that $\delta^{13}\text{C}_{\text{DIC}}$ of pore water registered
865 the leak earlier than significant increases in HCO₃⁻ concentration were detected¹²⁸. In these examples
866 the difference in $\delta^{13}\text{C}$ between baseline and injected CO₂ was 15 to 25 ‰. In these leakage
867 experiments the migration distance for the injected CO₂ is small (maximum 11 m – QICS) and it is
868 possible that the isotopic composition of the CO₂ could change during migration over the larger
869 distances associated with geological storage (kilometres deep). However, detailed modelling of
870 potential leakage at the QUEST CCS project, Edmonton, Canada, from the Basal Cambrian Sandstone

(BCS) storage reservoir into overlying aquifers indicated that the $\delta^{13}\text{C}_{\text{CO}_2}$ of the leaking CO_2 would differ from the injected CO_2 by less than 1 ‰⁵¹.

Another experiment released CO_2 with He and Kr tracers into the vadose zone of limestone and showed that molecular diffusivity was not an adequate model for coupled CO_2 - tracer behaviour; while He and Kr behaved according to predictive models, the CO_2 took significantly longer to travel through the substrate⁹⁶. This experiment gives weight to the hypothesis that noble gases may provide an early warning of CO_2 leakage. Further evidence suggesting that noble gases may be useful tracers of CO_2 migration comes from studies on natural CO_2 and gas seeps. At St John's, Arizona / New Mexico, USA, $\delta^{13}\text{C}$ was inconclusive in establishing the origin of elevated HCO_3^- in spring water, but He and Ne isotopes identified both mantle and crustal components and thus a deep origin for the CO_2 ¹²⁹. He and Ne isotopes were similarly used to confirm that elevated levels of soil-gas CO_2 and CH_4 were due to micro-seepage of gas from deep, hydrocarbon-bearing formations at Teapot Dome, Wyoming¹¹⁹. Importantly, this study established that total He concentrations of approximately just 10 ppm in soil gas and 0.1 ppm in groundwater aquifers would be sufficient to identify deep-sourced He¹¹⁹.

In summary, C-isotopes may be useful for detection of leakage and seepage if the baseline and injected CO_2 are significantly different. When isotopic compositions are not distinctive, combining $\delta^{13}\text{C}$ with CO_2 , O_2 and N_2 concentrations can help to constrain the CO_2 origin. Of the noble gases, He is a particularly sensitive leak and seep tracer due to its low background concentrations at the surface and likely high concentration in the storage reservoir, regardless of the He content of the injected CO_2 .

9. Summary, Implications and Conclusions:

The inherent stable isotope and noble gas composition of captured CO_2 has the potential to provide powerful monitoring tools for carbon capture and storage projects, both for in-reservoir processes and for identifying leakage and seepage from the storage unit. This application requires significant

compositional differences between the injected CO₂ and the reservoir (for in-reservoir monitoring) and between the reservoir plus injected CO₂ and overlying shallow aquifers, soil and atmosphere (for seepage monitoring).

In simplistic terms, captured CO₂ is generated in two stages: 1) initial reaction of a feedstock to produce a CO₂-bearing flue gas and 2) separation of the CO₂ from the other flue gases. When considering the likely isotopic and noble gas composition of the captured CO₂ stream, we found that the C-isotope composition and noble gas isotope ratios will be dominated by the initial feedstock, and noble gas concentrations will be controlled by the use of CO₂ purification technology.

For fossil fuel and C3 biomass feedstocks a $\delta^{13}\text{C}$ fractionation of -1.3 ‰ from the feedstock can be expected while the combustion of C4 biomass may result in greater isotope fractionation. There is a notable lack of information regarding the effect of CO₂ separation technologies (e.g. amine capture) on the stable isotope composition of captured CO₂ but ¹³C depletion by tens of permil is hypothetically possible. Combining hypothetical considerations with the small amount of available data suggests that C-isotope fractionation during amine capture will be between -20 and +3 ‰. This amounts to a total fractionation between the feedstock and the captured CO₂ of between -21 and +2 ‰. A lack of solubility data for noble gases in amine solvents and a lack of detailed noble gas measurements on captured CO₂ makes it difficult to predict the noble gas content. Fossil fuel feedstocks are likely to be enriched in radiogenic or terrigenous noble gases (especially ⁴He), and this isotopic component will be transferred to the CO₂, although any CO₂-purification processes are likely to cause noble gas depletion. However there is a growing body of evidence to suggest that oxyfuel CO₂ (and other processes that use cryogenic oxygen, such as Syngas plants) may be enriched in heavy noble gases Kr and Xe. While fossil fuels remain the dominant feedstock, CO₂ captured from power plants will likely have a high ⁴He content (at least before amine capture), but this will change over time if fossil fuels are increasingly replaced with biomass to provide renewable energy with potentially negative CO₂ emissions.

923

924 Likely baseline compositions for storage reservoirs and overlying aquifers, soil and atmosphere were
925 reviewed to assess the likelihood that injected CO₂ will be isotopically different and this is summarised
926 in Figure 3. Use of fossil fuels and C3 biomass feedstocks are most likely to produce captured CO₂ with
927 $\delta^{13}\text{C}$ distinctive from baseline conditions, although $\delta^{13}\text{C}$ of the CO₂ in some storage reservoirs may be
928 difficult to distinguish from coal or C3 biomass derived CO₂. CO₂ generated from C4 biomass,
929 fermentation, cement manufacture and natural gas processing will be more difficult to distinguish.
930 Elevated ⁴He concentrations that are expected to occur in various sources of captured CO₂ are unlikely
931 to contrast with storage reservoir baseline conditions due to the presence of radiogenic and terrigenous
932 ⁴He, but may provide a highly sensitive tracer for detecting leakage and seepage. Elevated Kr and Xe
933 in CO₂ captured from processes that use cryogenic oxygen may be useful, but there is not yet enough
934 data to assess how ubiquitous this enrichment is and whether the concentrations involved are
935 sufficient to allow detection in the reservoir. We note, however, that the wide range of noble gas
936 element and isotope ratios that can be measured means that detailed baseline characterisation of
937 reservoir and injected CO₂ is likely to yield some combination of noble gas ratios that provide a suitable
938 in-reservoir tracer.

939

940 A number of fundamental questions remain unanswered due to a lack of empirical data. While we
941 have tried to address these questions hypothetically, more research is necessary to test these
942 hypotheses. Specifically, 1) Will carbon capture technologies result in low noble gas concentrations
943 with preferential loss of light noble gases, and how much C-isotope fractionation will take place during
944 carbon capture? 2) Will CO₂ captured from oxyfuel plants have a higher noble gas content than amine-
945 captured CO₂, especially for heavy noble gases? 3) Will migration of the CO₂ plume over geological
946 distances result in significant fractionation of stable isotopes or noble gases, over what timescales and
947 distance will this fractionation be observed and how might this affect our ability to identify CO₂ leakage
948 or seepage?

949

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953 Supporting Information Available

954 Information regarding feedstock composition and gasification processes and supporting information
955 tables are provided in 1 × word document and 1 × excel spreadsheet. This information is available free
956 of charge via the Internet at <http://pubs.acs.org>.

957

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1347

Tables

Table 1. Summary of Noble Gas concentrations and solubilities

	Air (ppbv) ^a	Water (ppbv) ^b	Oil (mol ppb)	Gas (mol ppb)	Solubility in water ^e	Solubility in oil ^e
⁴ He	5,240	50	12,000 to 130,000 ^c	580 to 3,838,000 ^{e,f}	0.0090	0.0211
²⁰ Ne	18,180	181	2 to 21 ^c	4.1 to 1,294.4 ^{e,f}	0.0096	0.0198
⁴⁰ Ar	9,340,000	398,400	10,700 to 26,900 ^c	51,100 to 208,300 ⁶	0.036	0.0158
³⁶ Ar	31,607	1,348	1 to 151 ^d	20 to 11,849 ^{e,f}		
⁸⁴ Kr	650	51		1.6 to 120 ^{e,f}	0.0388	0.400
¹³⁶ Xe	8	0.9		0.1 to 5.7 ^{e,f}	0.0603	1.080

^a Calculated from Porcelli et al. (2002)¹⁰⁵. ^b Based on calculated equilibrium concentrations of elemental noble gases in low salinity water at 10 °C from Lake Baikal³², using the simplified assumption that 1 g of water = 1 cm³, and converted to isotopic abundances using isotopic ratios from Porcelli et al. (2002)¹⁰⁵. ^c Calculated from Ballentine et al (1996)⁸⁵; ^d Calculated from Torgersen and Kennedy (1999)⁸⁷; ^e calculated from Prinzhofer et al (2010)¹³⁰; ^f calculated from Kotarba et al (2014)¹³¹; ^g Solubilities¹³⁰ expressed as the ratio of the noble gas concentration in the liquid to the concentration in the gas (mol m⁻³ / mol m⁻³), at 50 °C and atmospheric pressure for water and heavy (API 25) oil.

Table 2. Expected C-isotope and noble gas compositions of the CO₂ stream generated by a variety of industrial and energy generating technologies, relative to their source components (feedstock, combustion atmosphere etc.) and with likely fractionations where relevant. Subsequent amine capture or physical absorption are not included. For processes that will be followed with amine capture (* in “Process” column), add: $\delta^{13}\text{C}$ enrichment of -20 to +2.5 ‰, and depletion of noble gas concentrations (especially light noble gases). For physical absorption in organic solvents (may or may not be used with all other processes), add a small positive C-isotopic enrichment, dependent on the relative efficiencies of the absorption and desorption processes, and depletion of noble gas concentrations (especially light noble gases). References for the C-isotope composition of feedstock and other components are given in the text and in the supplementary data tables, and values are summarised in Figure 1.

Process	Feedstock	$\delta^{13}\text{C}$ ‰ V-PDB of feedstock	$\delta^{13}\text{C}$ ‰ of process	$\delta^{13}\text{C}$ of CO ₂ ‰ V-PDB	Noble gas content of components	Noble Gases in CO ₂
Normal Combustion *	Coal	-30 to -20	-1.3	-31.3 to -21.3	High ⁴ He and ⁴⁰ Ar in fossil fuels. Atmospheric noble gases from air.	Air-like, plus enriched ⁴ He and ⁴⁰ Ar.
	Oil	-36 to -18		-37.3 to -19.3		
	Natural Gas	<-60 to -20		<-61 to -21.3		
	C3 biomass	-30 to -24	0	-30 to -24	Atmospheric noble gases	Air-like noble gases
	C4 biomass	-15 to -10	0 to +4	-15 to -6		
Oxyfuel	Coal	-30 to -20	-1.3	-31.3 to -21.3	High ⁴ He and ⁴⁰ Ar in fossil fuels. Heavy noble gases in cryogenic oxygen.	Enriched in heavy noble gases, ⁴ He and ⁴⁰ Ar.
	Oil	-36 to -18	-1.3	-37.3 to -19.3		
	Natural Gas	<-60 to -20	-1.3	<-61 to -21.3		
	C3 biomass	-30 to -24	0	-30 to -24	Heavy noble gases in cryogenic oxygen.	Enriched in heavy noble gases.
	C4 biomass	-15 to -10	0 to +4	-15 to -6		
Gasification / Syngas	Coal	-30 to -20	Difficult to predict. Possible small -ve ‰	<-30 to <-20	High ⁴ He and ⁴⁰ Ar in fossil fuels. Use of steam will add atmospheric noble gases. Use of cryogenic O ₂ will add heavy noble gases.	Atmospheric noble gases. Possibly enriched in heavy noble gases. High ⁴ He and ⁴⁰ Ar for fossil fuel feedstocks.
	Oil	-36 to -18		<-36 to <-18		
	Natural Gas	<-60 to -20		<-60 to <-20		
	C3 biomass	-30 to -24		<-30 to <-24		
	C4 biomass	-15 to -10		<-15 to <-10		
Synfuel / chemical plant	Coal	-30 to -20	Possible small +ve ‰	>-30 to >-20	Increased likelihood of using cryogenic O ₂ will add heavy noble gases	Air like ratios and likely enriched in heavy noble gases
	Oil	-36 to -18		>-36 to >-18		
	Natural Gas	<-60 to -20		>-60 to >-20		
Fermentation	C4 Sugars	-15 to -10	+4 to +6	-11 to -4	Air saturated water	Air-like ratios, depleted concentrations relative to air.
Cement *	Coal + Limestone	-30 to -20 0	-1.3 for coal + mixing	-16 to -11	High ⁴ He and ⁴⁰ Ar in fossil fuels. Atmospheric noble gases from air. Heavy noble gas enrichment for oxyfuel.	Air-like, plus enriched ⁴ He and ⁴⁰ Ar. Heavy noble gas enrichment for oxyfuel.
Steel Industry: ISP *	Coal	-30 to -20	-1.3	-31.3 to -21.3	High ⁴ He and ⁴⁰ Ar in fossil fuels. Atmospheric noble gases from air.	Air-like, plus enriched ⁴ He and ⁴⁰ Ar.
Steel Industry: DRI	As for Syngas Iron ore	As for Syngas			High ⁴ He and ⁴⁰ Ar in iron oxide. Atmospheric noble gases from air. Heavy noble gases in cryogenic oxygen?	Air-like, plus enriched ⁴ He and ⁴⁰ Ar. Possibly enriched in heavy noble gases.
Natural gas processing (Amine capture)	CO ₂ co-existing with natural gas	-14 to +14	-20 to +2.5	-34 to +21	High ⁴ He and ⁴⁰ Ar in natural gas.	Noble gases likely lost during capture. Preferential retention of heavy noble gases. Radiogenic and terrigenous isotope ratios retained but abundances << air.

Figures

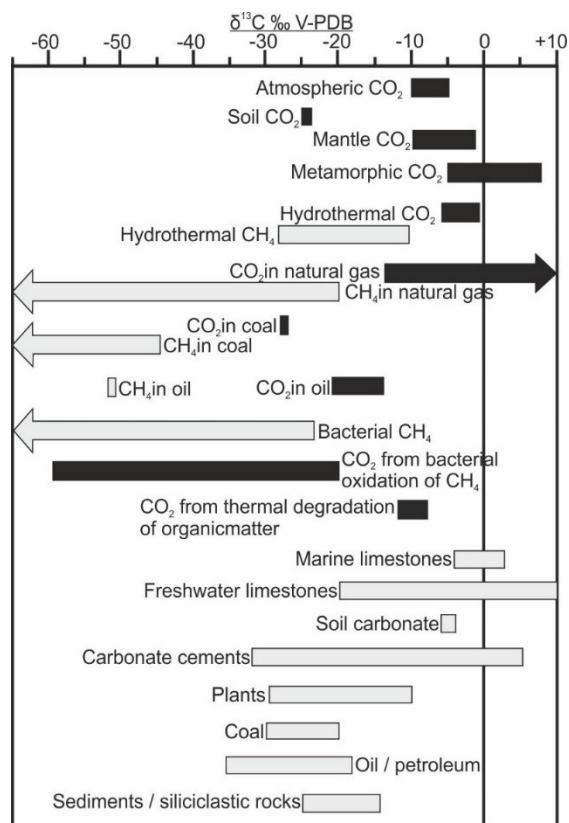


Figure 1. C-isotope values for a range of naturally occurring materials. Black boxes indicate CO_2 . Grey boxes are other substances. Arrows represent values off the scale of the diagram. See Supplementary data Table S1 for references. Note that a wide range of $\delta^{13}\text{C}$ values are covered by naturally occurring CO_2 sources.

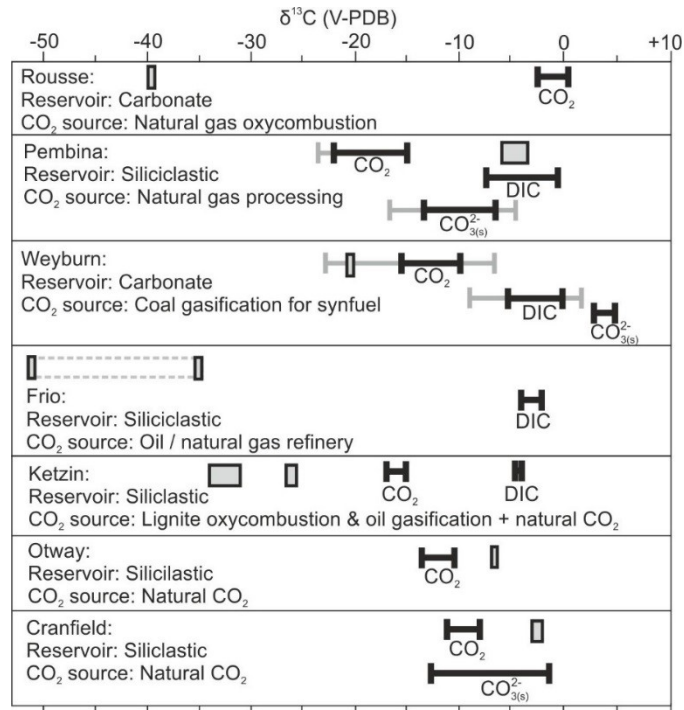


Figure 2: Comparison of injected CO₂ δ¹³C values with reservoir baseline CO₂, DIC and carbonate minerals in existing CCS projects. Grey boxes show the δ¹³C of injected CO₂; Frio and Ketzin show 2 boxes each to reflect the two anthropogenic CO₂ sources used in these projects. Reservoir baseline values for CO₂, DIC and carbonate minerals are shown by horizontal crosshair lines. Where the baseline data are variable, the full range in values is shown by grey lines while the majority of data are represented by black lines. See Tables S2-S4 for references.

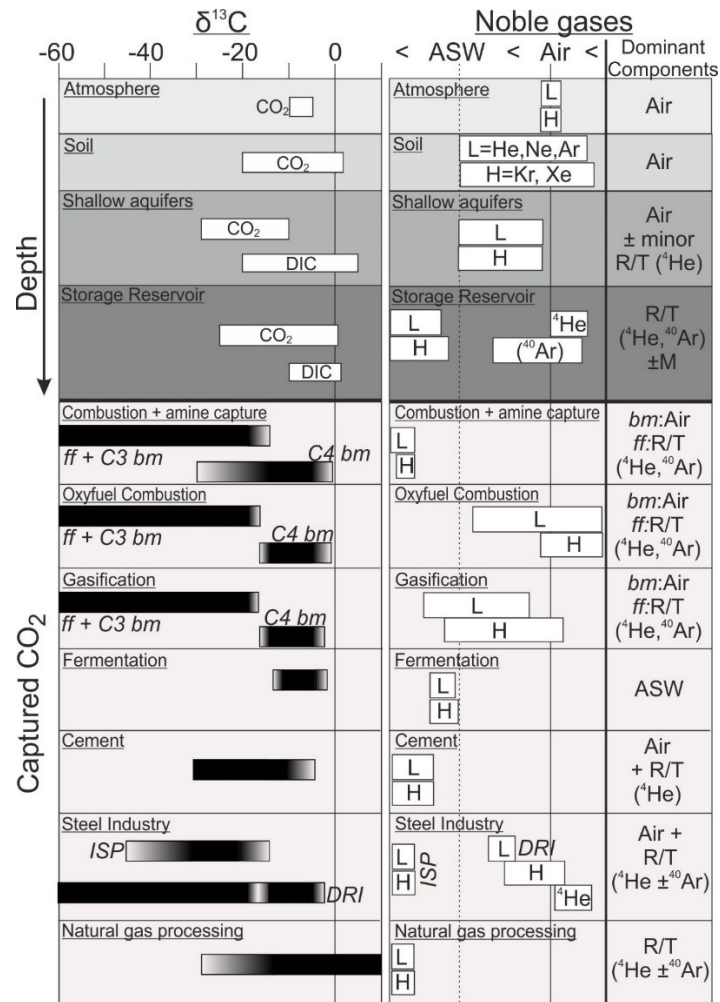


Figure 3. Comparison of the range of inherent tracer values for storage and leakage reservoirs (Tables S1-S6), and the expected captured CO₂ composition for various CO₂ sources (Table 2). Boxes represent the range of $\delta^{13}\text{C}$ (V-PDB) and noble gas concentration (relative to air and ASW) in baseline conditions for atmosphere, soil, shallow aquifers and storage reservoirs, compared to the range of values expected for different sources of captured CO₂. C-isotopes are given in δ notation relative to V-PDB. Noble gases shown for absolute concentrations relative to air and ASW, with dominant components resolvable by isotopic analysis; “L” = light noble gases, “H” = heavy noble gases, “R/T” = radiogenic and / or terrigenous component, “M” = mantle component, “ASW” = air saturated water. *ff* = fossil fuels; *bm* = biomass; *ISP* = integrated steel plant; *DRI* = directly reduced iron.